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# Singly Unified Driving Force Dependence of Outer-Sphere Electron-Transfer Pathways of Nonheme Manganese(IV)-Oxo Complexes in the Absence and Presence of Lewis Acids

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Supporting Information

ABSTRACT: Epoxidation of styrene derivatives, sulfoxidation of thioanisole derivatives, and hydroxylation of toluene derivatives by a nonheme manganese(IV)-oxo complex binding triflic acid, [(N4Py)- $Mn^{IV}(O)$ <sup>2+</sup>-(HOTf)<sub>2</sub> [1-(H<sup>+</sup>)<sub>2</sub>], and scandium triflate,  $[(N4Py)Mn^{IV}(O)]^{2+}-(Sc(OTf)_3)_2 [1-(Sc^{3+})_2],$  occur via outer-sphere electron-transfer (OSET) pathways, exhibiting singly unified driving force dependence, enabling one to predict absolute values of the second-order rate constants of these three types of substrate oxidations by the manganese(IV)-oxo complex, using the Marcus theory of electron transfer. When  $[(N4Py)Mn^{IV}(O)]^{2+}$ (1) was replaced by  $[(N4Py)Fe^{IV}(O)]^{2+}$  (2), OSET pathways were changed to inner-sphere electron-transfer (ISET) pathways. The difference in the OSET versus ISET pathways is clarified based on the difference in the Lewis basicity of the oxo moieties in 1 and 2.

Ater oxidation to dioxygen and the reverse reaction, i.e., dioxygen reduction to water, are critical redox reactions for biological energy conversions, in which proton-coupled electron transfer (PCET) plays a pivotal role.<sup>1-4</sup> The binding or release of redox-inactive metal ions, such as scandium ion  $(Sc^{3+})$ , acting as Lewis acids as well as protons can also couple with electron transfer (ET), referred to as a metal-ion-coupled electron transfer (MCET). $5^{-13}$  Ever since Sc<sup>3+</sup> was shown to be bound to the oxo moiety of an iron-oxo complex,<sup>1</sup> extensive efforts have been devoted to investigating the MCET pathways of not only metal-oxo species but also metal-peroxo and -superoxo species in relation with the corresponding PCET pathways.<sup>14-21</sup> We have recently reported that different types of redox reactions, such as epoxidation, sulfoxidation, and hydroxylation of styrene, thioanisole, and toluene derivatives by  $[(N4Py)Mn^{IV}(O)]^{2+}-(HOTf)_2$  [1- $(H^+)_2$ ; N4Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine], proceed via rate-determining outer-sphere electron transfer (OSET) from substrates to  $1-(H^+)_2$ .<sup>6</sup> log  $k_2$ (where  $k_2$  is the observed second-order rate constant) by 1- $(H^+)_2$ , and PCET from one-electron reductants to  $[(N4Py)-Mn^{IV}(O)]^{2+}$  (1) in the presence of HOTf shows a remarkably unified ET driving force dependence in light of the Marcus

theory of ET, which allows us to predict the absolute rate constants by knowing the one-electron oxidation potentials of substrates.<sup>6</sup> However, there has so far been no direct comparison of the PCET and MCET pathways of different metal-oxo species in terms of the ET driving force dependence of the PCET and MCET rate constants.<sup>2</sup>

We report herein the singly unified ET driving force dependence of the logarithm of the rate constants of MCET and PCET reactions of  $[(N4Py)Mn^{IV}(O)]^{2+}-(Sc(OTf)_3)_2$  [1- $(Sc^{3+})_2$  and 1- $(H^+)_2$ , 7,15 respectively, as OSET reactions in light of the Marcus theory of ET (Scheme 1).28 The singly





unified ET driving force dependence of the logarithm of the rate constants of MCET and PCET reactions of 1-(Sc3+)2 and  $1-(H^+)_2$  is compared with the ET driving force dependence of the logarithm of the rate constants of PCET reactions of  $[(N4Py)Fe^{IV}(O)]^{2+}$  (2) to clarify the difference in the Lewis basicity of the oxo moieties in 1 and 2.

 $1-(Sc^{3+})_2$  was synthesized by the addition of Sc(OTf)<sub>3</sub> to a 1:1 mixed solution of trifluoroethanol (TFE) and acetonitrile (MeCN) containing 1 at 273 K according to the literature procedure.<sup>15,16</sup> One Sc(OTf)<sub>3</sub> molecule binds with the oxo moiety, and the other  $Sc(OTf)_3$  molecule binds with the OTf moiety of  $Sc(OTf)_3$  binding to the oxo moiety.<sup>15</sup> The binding of two  $Sc(OTf)_3$  molecules in  $1-(Sc^{3+})_2$  results in a weak interaction with electron-donor substrates, providing an

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excellent opportunity to investigate OSET pathways, which require only weak interaction between an electron donor (oneelectron reductant) and acceptor (one-electron oxidant).

Epoxidation of *trans*-stilbene with 1 was reported to proceed slowly with the second-order rate constant of  $1.6 \times 10^{-2}$  M<sup>-1</sup> s<sup>-1</sup> in TFE/MeCN (1:1) at 273 K.<sup>6</sup> When 1 was replaced by 1-(Sc<sup>3+</sup>)<sub>2</sub>, the epoxidation rate of *trans*-stilbene became 280 times faster to afford the rate constant of 4.4 M<sup>-1</sup> s<sup>-1</sup> (Figure S1). The rate constants of oxidation of other styrene derivatives with 1-(Sc<sup>3+</sup>)<sub>2</sub> were also determined (Table S1).

The observed second-order rate constants of oxidation of styrenes with  $1-(Sc^{3+})_2$  are compared with those of OSET from one-electron reductants to 1,  $1-(Sc^{3+})_2$ , and  $1-(H^+)_2$  by the Marcus theory of adiabatic OSET (eq 1).<sup>28</sup> The driving forces  $(-\Delta G_{et})$  of OSET are obtained from the one-electron-reduction potentials ( $E_{red}$  vs SCE) of one-electron oxidants, 1 (0.80 V),<sup>16</sup>  $1-(Sc^{3+})_2$  (1.42 V),<sup>16</sup> and  $1-(H^+)_2$  (1.65 V),<sup>7</sup> and the one-electron-oxidation potentials ( $E_{ox}$  vs SCE) of one-electron reductants using eq 2.

$$k_{\rm et} = Z \, \exp[-(\lambda/4)(1 + \Delta G_{\rm et}/\lambda)^2/k_{\rm B}T] \tag{1}$$

$$-\Delta G_{\rm et} = -e(E_{\rm ox} - E_{\rm red}) \tag{2}$$

The ET driving force dependence of log  $k_{\rm et}$  of OSET from ferrocene derivatives to 1 and from coordinatively saturated metal complexes to  $1-({\rm Sc}^{3+})_2$  and  $1-({\rm H}^+)_2$  is well fitted by the Marcus equation of OSET (eq 1)<sup>28</sup> using the identical value of the reorganization energy of ET ( $\lambda = 2.16$  eV), as shown in Figure 1.<sup>7,16</sup> The Z value (normally  $1.0 \times 10^{11}$  M<sup>-1</sup> s<sup>-1</sup>)<sup>29</sup> of OSET indicates that the formation constant (K) value of the OSET reactions is ca. 0.02 M<sup>-1</sup> because of little interaction in the precursor complexes for OSET reactions of electron-donor complexes with 1-(Sc<sup>3+</sup>)<sub>2</sub> and 1-(H<sup>+</sup>)<sub>2</sub>.

The log  $k_{ox}$  values of the oxidation of styrenes and thioanisoles with  $1-(Sc^{3+})_2$  [black open circles (nos. 1-4) and red open triangles (nos. 6-10) in Figure 1, respectively] agree remarkably well with the log  $k_{\rm et}$  values of OSET from one-electron donors [i.e., ferrocene derivatives (pink closed circles, nos. 24-27) and coordinatively saturated metal complexes (blue open and closed squares, nos. 15-23) to 1,  $1 - (Sc^{3+})_2$ , and  $1 - (H^+)_2$  (black line in Figure 1)]. Thus, the oxidation of styrenes and thioanisoles by  $1-(Sc^{3+})_2$  and  $1-(H^+)_2$  as well as the hydroxylation of toluene derivatives<sup>30</sup> by  $1-(H^+)_2$ (green open circles, nos. 11-14) proceed via OSET from electron-donor substrates (i.e., styrenes, thioanisoles, and toluene derivatives) to  $1-(Sc^{3+})_2$  and  $1-(H^+)_2$ , as shown in Scheme 2. OSET from an organic substrate (S) to  $1-(Sc^{3+})_2$ occurs as the rate-determining step, following the precursor complex formation, followed by oxygenation of S<sup>++</sup> to produce the oxidized organic product (SO) with manganese(II) species, accompanied by the release of two  $Sc^{3+}$  ions. In the case of  $1-(H^+)_2$  as well, OSET from S including toluene derivatives to  $1-(H^+)_2$  is the rate-determining step. The OSET pathway of  $1-(Sc^{3+})_2$  and  $1-(H^+)_2$  may result from the steric effects of two Sc(OTf)<sub>3</sub> and two HOTf molecules, respectively, which bind to 1, precluding inner-sphere interaction between 1 and electron-donor substrates.

The ET driving force dependence of log  $k_{\rm et}$  of OSET from one-electron reductants to **2** in the absence and presence of Sc(OTf)<sub>3</sub> and HOTf is shown in Figure 2, where the reorganization energy of ET ( $\lambda = 2.74$  eV, blue line) to fit all of the OSET data is larger than that of **1** in the absence and presence of HOTf. In contrast to the case of **1**-(H<sup>+</sup>)<sub>2</sub>, the log



Figure 1. Unified ET driving force  $(-\Delta G_{et})$  dependence of the logarithm of the observed second-order rate constants (log  $k_{ox}$ ) for the oxidation of styrenes<sup>6</sup> [(1) 4-methoxystyrene, (2) trans-stilbene, (3) *cis*-stilbene, (4) 4-methylstyrene, and (5) styrene] by  $1-(Sc^{3+})_2$ (black open circles) and  $1-(H^+)_2$  (black closed circles), sulfoxidation of *p*-X-substituted thioanisoles, <sup>7,15</sup> [X = (6) MeO, (7) H, (8) F, (9) Br, and (10) CN] with  $1-(Sc^{3+})_2$  (red open triangles) and  $1-(H^+)_2$ (red closed triangles), and C-H bond activation of toluene derivatives<sup>8,30</sup> [(11) hexamethylbenzene, (12) pentamethylbenzene, (13) durene, and (14) mesitylene] with  $1-(H^+)_2$  (green open circles) and log  $k_{\rm et}$  for ET from various one-electron reductants<sup>16</sup> [(15)  $\begin{bmatrix} \text{re}^{\text{II}}(\text{Me}_{2}\text{phen})_{3}]^{2+}, \ (16) \ [\text{Fe}^{\text{II}}(\text{Ph}_{2}\text{phen})_{3}]^{2+}, \ (17) \ [\text{Fe}^{\text{II}}(\text{bpy})_{3}]^{2+}, \ (18) \ [\text{Fe}^{\text{II}}(5\text{-}\text{Clphen})_{3}]^{2+}, \ (19) \ [\text{Ru}^{\text{II}}(\text{bpy})_{3}]^{2+} \ (20) \ [\text{Ru}^{\text{II}}(\text{Me}_{2}\text{bpy})_{3}]^{2+}, \ (21) \ [\text{Ru}^{\text{II}}(5\text{-}\text{Clphen})_{3}]^{2+}, \ (22) \ [\text{Ru}^{\text{II}}(5\text{-}\text{Srbpy})_{3}]^{2+}, \ and \ (23) \ [\text{Ru}^{\text{II}}(5\text{-}\text{NO}_{2}\text{phen})_{3}]^{2+} \ to \ 1\text{-}(\text{Sc}^{3+})_{2} \ (blue$ open squares) and  $1-(H^+)_2$  (blue closed squares) in TFE/MeCN (v/v 1:1) at 273 K. The pink closed circles exhibit the ET driving force dependence of log  $k_{et}$  for ET from one-electron reductants [(24) ferrocene, (25) bromoferrocene, (26) acetylferrocene, and (27) 1,1'dibromoferrocene] to 1 in TFE/MeCN (v/v 1:1) at 273 K.<sup>1</sup>

## Scheme 2. Oxygenation of Substrates by $1-(Sc^{3+})_2$ via OSET



 $k_{\rm ox}$  values for sulfoxidation of thioanisoles and C–H bond activation of toluene derivatives with **2** in the presence of Sc(OTf)<sub>3</sub> and HOTf (10 mM; nos. 1–5, black open and closed circles in Figure 2, respectively) are ~3 orders magnitude higher than the log  $k_{\rm et}$  values of OSET with the same ET driving force. The larger  $k_{\rm ox}$  values than the  $k_{\rm et}$  values with the same ET driving force result from the inner-sphere



Figure 2. Plots of the logarithm of the observed second-order rate constants (log  $k_{ox}$ ) for sulfoxidation of p-X-substituted thioanisole derivatives [X = (1) Me, (2) H, (3) Cl, (4) Br, and (5) CN] by 2 in the presence of Sc(OTf)<sub>3</sub> (10 mM; black open circles) and HOTf (10 mM; black closed circles), C-H bond activation of toluene derivatives [(6) hexamethylbenzene, (7) pentamethylbenzene, (8) durene, (9) 1,2,4-trimethylbenzene, (10) p-xylene, and (11) mesitylene] by 2 in the presence of  $Sc(OTf)_2$  (10 mM; red open circles) and HOTf (10 mM; red closed circles) versus the ET driving force  $(-\Delta G_{\rm et})$ ,<sup>17,30</sup> with the ET driving force dependence of log  $k_{\rm et}$ for OSET from various one-electron reductate of log  $\kappa_{et}$ for OSET from various one-electron reductates [(12)  $[Fe^{II}(Ph_2phen)_3]^{2+}$ , (13)  $[Fe^{II}(bpy)_3]^{2+}$ , (14)  $[Ru^{II}(4,4'-Me_2phen)_3]^{2+}$ , (15)  $[Ru^{II}(5,5'-Me_2-phen)_3]^{2+}$ , (16)  $[Fe^{II}(5-Clphen)_3]^{2+}$ , and (17)  $[Ru^{II}(bpy)_3]^{2+}$ ] to 2 in the presence of HOTf (10 mM; blue open circles) in MeCN at 298 K.<sup>17</sup> The blue closed circles show the driving force dependence of log  $k_{et}$  for ET from one-electron reductants [(18) decamethylferrocene, (19) octamethylferrocene, (20) 1.1'-dimethylferrocene, (21) n-amylferrocene, and (22) ferrocene] to 2 in the absence of HOTf in MeCN at 298 K.

nature of the PCET pathway, in which the interaction between organic electron-donor substrates and **2** in the presence of HOTf (10 mM) is significantly larger than that between the same substrates and 1-(H<sup>+</sup>)<sub>2</sub>.<sup>31</sup> In fact, the formation constants of the precursor complex between durene and **2** in the presence of HOTf (10 mM) were determined to be  $1.2 \times 10^2$  M<sup>-1</sup>, which is much larger than that of typical OSET reactions (ca. 0.02 M<sup>-1</sup>).<sup>17</sup> It should be noted that two Sc(OTf)<sub>3</sub> or two HOTf molecules are bound to **1** to produce 1-(Sc<sup>3+</sup>)<sub>2</sub> or 1-(H<sup>+</sup>)<sub>2</sub>, respectively, but no binding of Sc(OTf)<sub>3</sub> or HOTf to **2** was observed prior to ET.

The strong binding of  $Sc(OTf)_3$  or HOTf to the oxo moiety in 1, which shows sharp contrast to the very weak binding of  $Sc(OTf)_3$  or HOTf to that in 2, indicates that the oxo moiety in 1 should be more basic than that in 2, which may result from the smaller electronegativity of manganese (2.05 mdyn) than that of iron (2.31 mdyn),<sup>32a</sup> as well as the smaller electrophilicity index of manganese (0.93) than that of iron (1.05).<sup>32b</sup> Density functional theory calculations on both 1 and 2 also revealed that Mn<sup>IV</sup>(O) species with a higher negative charge of -0.81 on the oxo moiety show higher basicity than  $Fe^{IV}(O)$  species with a lower negative charge of -0.52 on the oxo moiety (see the Experimental Section and Table S2). Furthermore, the binding energy of a proton to these two metal oxo species has also been calculated, indicating that the proton affinity of 1 is stronger in energy than that of 2 by 13.22 kcal  $mol^{-1}$  (Table S2).

In conclusion, the epoxidation of styrenes, sulfoxidation of thioanisoles, and C-H bond activation of toluene derivatives with  $1-(Sc^{3+})_2$  and  $1-(H^+)_2$  proceed via the rate-determining OSET reactions, which exhibit the singly unified ET driving force dependence of the logarithm of the observed secondorder rate constants, which is fitted well by using the Marcus theory of OSET (Figure 1), enabling us to predict the absolute values of the rate constants by knowing only the one-electron redox potentials of the reactants. In contrast to 1, the oxidation of thioanisoles and C-H bond activation of toluene derivatives with 2 in the presence of  $Sc(OTf)_3$  and HOTf proceed via the rate-limiting inner-sphere electron-transfer (ISET) reactions, in which the formation constant (K) of the precursor complex between the organic substrates and 2 in the presence of HOTf is significantly larger than that between the same substrates and  $1-(H^+)_2$ . Such a difference in the PCET reactivity between 1 and 2 results from the higher basicity of the oxo moiety in 1 than in 2. This study provides an important step forward to fill the gap between the OSET pathways and the reactions of cationic electrophiles and neutral nucleophiles through ISET pathways.<sup>33,3</sup>

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02403.

Experimental section, Tables S1 and S2, and Figures S1 and S2 (PDF)

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#### Notes

The authors declare no competing financial interest.

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